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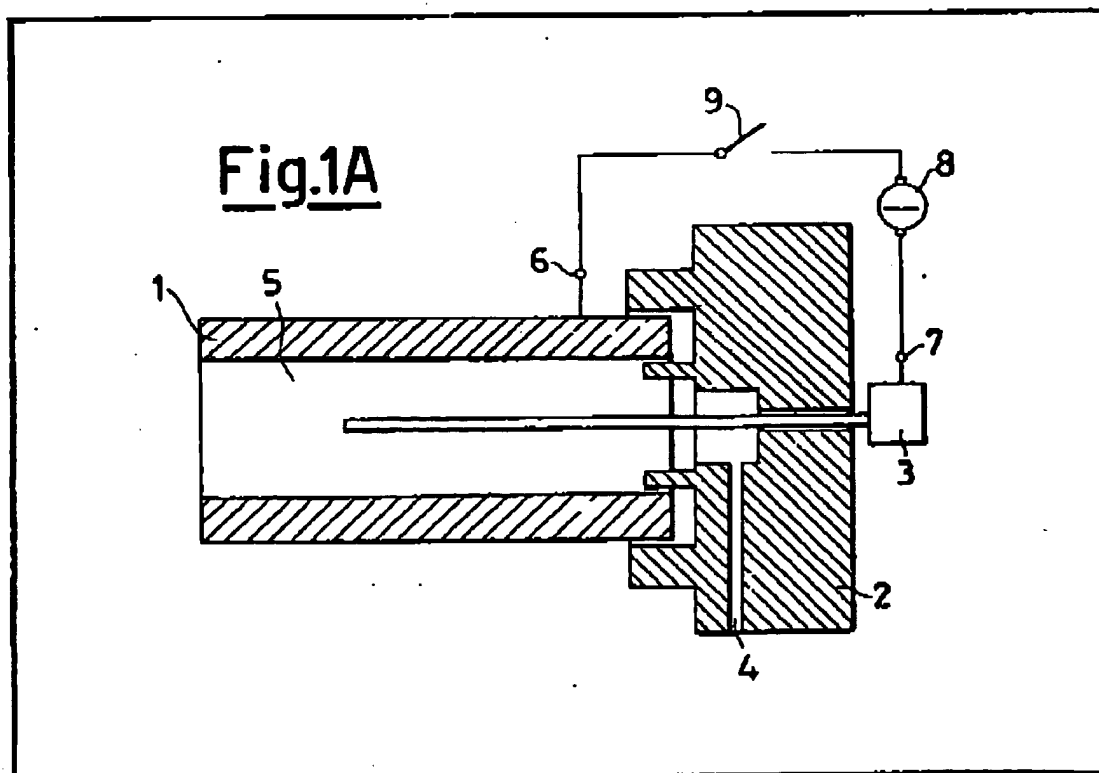
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method or by an equivalent spectro-
metric method.

(54) Determination of metal in gas

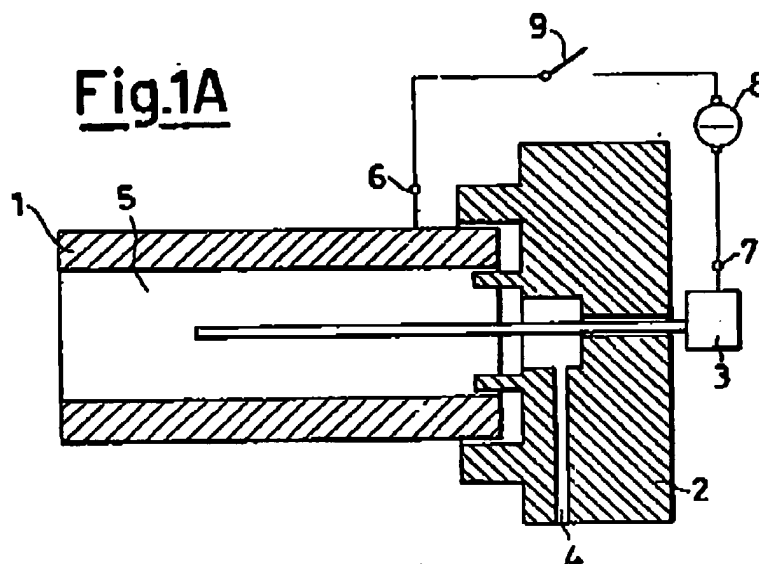
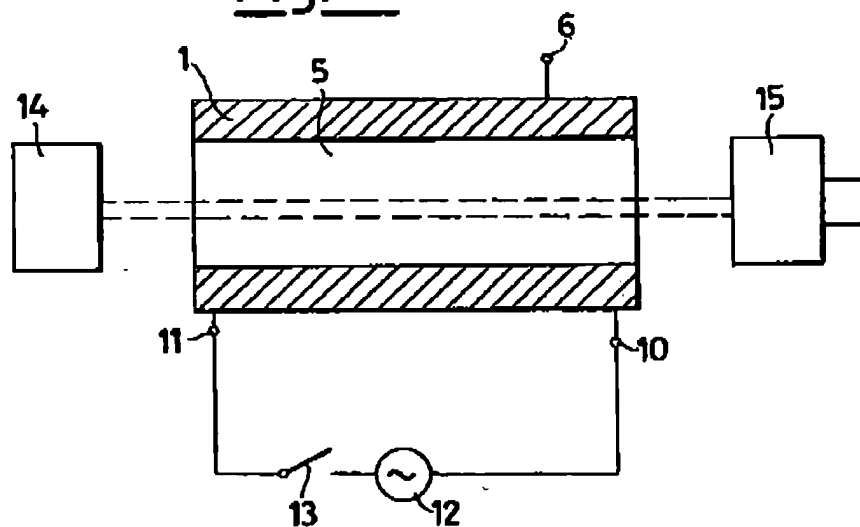
(57) To determine the metal content, e.g. the lead content, of a gas such as air, the gas is passed into the cavity (5) of a cylinder (1) having an electrode (3) disposed along its axis. A high electrical potential is applied between the cylinder (1) and the electrode (3) by means of a direct current generator (8), and the resulting electrostatic field causes particles dispersed in the gas to be deposited upon the walls of the cavity (5). The cylinder (1) is then heated to vaporise the deposited particles, and the metal content of the vapour is then determined by an electrothermal atomic absorption



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Fig.1AFig.1B

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SPECIFICATION

Determination of the metal content of gases

- 5 This invention relates to a method and apparatus for quantitatively determining the metal content of a gas or a gaseous mixture.
- 10 Gases generally contain varying amounts of solid and/or liquid constituents in dispersion, which constituents are removable with varying degrees of difficulty depending upon the particle size. A typical example of such gas is the earth's atmosphere itself, which generally contains solid dust constituted by lithoid material of natural origin (e.g. the products of wind erosion and volcanic emissions) and industrial origin (e.g. smoke, dust and sublimates). The composition, nature and quantity of the particles can vary within very wide limits, and can have harmful effects both on man and living beings in general, and on the environment.
- 20 Current and proposed legislation on this subject deals with this problem, and limits are set on harmful emissions in order to restrict the phenomenon, at least with regard to industrial activity. For example, the E.P.A. (Environment Protection Agency) proposes a limit for the U.S.A. on the lead content in the atmosphere, this limit being 1.5 micrograms per cubic metre of air, equal to about 1.2 parts per thousand and million. It is believed that limits of the same order of magnitude will be set in the future for the other heavy metals. These metals are very harmful to living beings even if assimilated in small quantities because they accumulate, and because over a period of time they can be transmitted to man himself through the alimentary chain.
- 40 It is therefore very important to qualitatively and quantitatively determine these elements in the atmosphere and in other gases in which they are present, even in a very small quantity, and the method and apparatus of the invention are suitable for this purpose.
- 45 The method and apparatus according to the invention can also be advantageously used for analysing industrial gases in production processes to provide accurate results which can be used for controlling the production process itself. Known methods for such analyses generally consist of a preliminary stage of concentration of the particles in the gases. This is done by passing the gas through suitable collection filters of known porosity so as to accumulate a substantial quantity of dust, sufficient to enable the required analyses to be made on the material collected. The collected material is recovered from the filter and then analysed. Such a mechanical separation, using apparatus of varying sophistication, is not of high efficiency because it is inevitably influenced by the size distribution of the particles. The time required for taking the sample is also necessarily long, and the filters themselves

can be a source of analysis error in that they can themselves contain the elements which are to be determined. The analysis is complicated because the enriched material sampled by the collection apparatus has to be transferred to the analysis apparatus after any required intermediate treatment. An analysis carried out by the aforesaid methods is generally of poor reproducibility and contains systematic errors, as the operators are required to carry out a series of operations which naturally involve the possibility of error.

- 70 According to the present invention, there is provided a method of quantitatively determining the metal content of a gas, which metal is dispersed in the gas as particles comprising the metal, which method comprises passing the gas into a cavity in which is housed an electrical conductor supplied with direct current whereby an electrostatic field is generated between the electrical conductor and the walls of the cavity and whereby particles dispersed in the gas are deposited upon the walls of the cavity by the action of the electrostatic field; heating the walls of the cavity to vaporise the deposited particles; and determining the metal content of the vapour by an electrothermal atomic absorption method or by a spectrometric method.

- 95 In an embodiment of the method according to the invention, the dust contained in the gas to be analysed is deposited directly onto the inner walls of the cavity, in the centre of which there is an electrical conductor subjected to a high potential direct current, and through which the gas to be analysed is passed. The cavity walls are connected either to the opposite pole of the electrical generator or to earth.
- 105 In a preferred embodiment, the cavity is constituted by the interior of a hollow cylindrical body constructed of an electrically conducting material resistant to temperature, and the central conductor is of elongated shape and capable of generating a high electrical field per unit of surface area. The electrical field thus generated permits very efficient collection, which is not influenced to any great extent by the particle size distribution. In this respect, it is possible to collect a sufficient quantity of dust in a short time, i.e. a time which usually does not exceed a few hundred seconds.

- The material collected in the cavity on its inner surface is analysed quantitatively by measuring the absorption using an electrothermal atomic absorption method. This method consists of raising the temperature of the cavity, for example to a temperature of from 1000 to 2500°C, while the cavity is located in the optical path of an atomic spectrometer in which is located a source for analysing the chemical element to be determined. Alternatively, a spectrometric method can be used.
- 130 The determination method according to the

invention is advantageous in that it is not influenced to any substantial extent by the size distribution of the dust, and is able to quickly supply reproducible quantitative results. It is not necessary to handle the sampled particles, as the same cavity can serve for the collection and the analysis, without any intermediate operations on the collected particles.

For a better understanding of the invention reference will now be made, by way of example, to the accompanying drawing, Figs. 1A and 1B of which illustrate respectively the particle collection and analysis steps of the method of the invention.

The apparatus shown in Fig. 1A consists of a hollow cylinder 1 of circular cross-section onto which an electrically insulating cap 2, supporting an electrode 3, is fitted. The cap 2 has an aperture 4 for discharging the gas to be analysed which flows into cavity 5 and grazes the elongated part of the electrode 3. By means of electrical connections 6 and 7 and a high potential direct current generator 8, a high potential difference of from 800 to 5000 V is maintained between cylinder 1 and electrode 3 when switch 9 is closed. This voltage range is the preferred range, although it is possible to use voltages outside of this range, but at decreased efficiency. The time for which the gas remains in the apparatus is from 0.02 to 2 seconds, preferably from 0.1 to 0.5 seconds. The ratio of the length to the diameter of the cavity 5 is from 5:1 to 50:1, preferably from 8:1 to 20:1.

When the required amount of dust has been deposited in the cavity 5, the connection 6 is broken, and the cap 2 and the electrode 3 are removed, whereby the apparatus is as shown in Fig. 1B. The cylinder 1 is raised to high temperature so that the deposited material vaporises and diffuses into the cavity and out of it. The required temperature is generally between 1000 and 2500°C, and in a preferred embodiment this is obtained by connecting the cylinder 1 to a current generator 12 by means of connections 10 and 11, and closing switch 13. Due to the resistance of the cylinder 1, it is heated to the required temperature by the Joule effect. A hollow cathode lamp 14 generates a light beam which traverses the cavity 1 in which the atomic vapour formed causes a reduction in intensity which is detected by a photomultiplier monochromator 15 which gives the required analytical data with respect to the quantity of gas which was made to flow through the cavity 5 during the first stage. Lamp 14 and monochromator 15 can be replaced by atomic absorption spectrometers of the types known in the art.

Measurements have been carried out using an apparatus as shown in Figs. 1A and 1B, the cylinder being a hollow graphite cylinder of length 35 mm, outer diameter 4.6 mm and

inner diameter 3 mm. Lead measurement was carried out in an enclosed environment in the Analytical Chemistry Laboratory of the University of Bari, which is located at about 50

metres from an urban road carrying high-density automobile traffic. Zinc and copper measurements were carried out by placing the apparatus in a mechanical workshop in which these metals were being machined. The apparatus was calibrated by placing known quantities of the element to be measured in the cavity using known volumes of solution with a known concentration of the element to be determined, and by using electrothermal atomic absorption measurement.

All three of the aforesaid elements were deposited by inserting the cap 2 and electrode 3 into the cylinder 1, and passing the gas to be sampled through the cavity 5 by drawing a known quantity of gas through the aperture 4 using a vacuum pump. The flow rate was 8.2×10^{-4} l/sec. The potential applied was 1500 V D.C. The time for which the gas was drawn through the aperture 4 varied according to the concentration of the element in question, but in no case did it exceed 10 minutes.

The electrical contacts were then broken and the cap 2 and electrode 3 were removed. An atomic absorption measurement was then made in accordance with the required method for the element to be determined. Analytical data was obtained by measuring the height of the absorption peak or its area. An area measurement gives a more accurate value. The calibration graphs obtained by measuring the area were linear as far as 10^{-11} g for lead and zinc, whereas in the case of copper the values were already non-linear at this level. In the case of lead, the determined values lay between 0.1 and 0.3 $\mu\text{g}/\text{m}^3$, for zinc between 1 and 5 $\mu\text{g}/\text{m}^3$ and for copper between 0.01 and 1 $\mu\text{g}/\text{m}^3$. The analyses were repeated, and the values were found to be fully reproducible. The time required for a measurement was between 5 and 20 minutes.

The theory of electrostatic precipitation dictates that the total precipitation obtainable is an asymptotic value which is attainable by increasing the potential, reducing the volumetric throughput or elongating the cylinder. The precipitation obtained under the aforesaid conditions was that corresponding to the asymptotic value.

By way of comparison, measurements were made by interposing filters having an average porosity of 0.2 μ in the gas flow, these filters being those normally suitable for sampling by the analysis methods known in the art. Downstream of these filters, absorption values of 10–20% with respect to the unfiltered atmosphere were obtained. This indicates that even with the best filters available, 10–20% is lost, and analyses carried out by the known methods contain errors of this order of magnitude.

As is apparent from the above, the method according to the invention is simple and fast, and the apparatus may be of limited overall size and low cost, one of the reasons being that high-value materials are not required. For the hollow cylinder 1, for which good electrical conductivity, mechanical strength, chemical inertia and temperature resistance are required, graphite has proved to be particularly suitable, a further reason being that it is suitable for heating by the Joule effect. If other heating systems are used, this material can be replaced by a metal having a high melting point, such as tungsten, tantalum or molybdenum.

For reasons of simplicity, the description given above has related to the method applied to the analysis of a single element at a time, it being necessary to use a particular type of hollow cathode lamp 14 for each element required. However, if a number of elements are to be determined simultaneously, a multi-element hollow cathode lamp 14 and a suitable polychromator 15 are used.

CLAIMS

1. A method of quantitatively determining the metal content of a gas, which metal is dispersed in the gas as particles comprising the metal, which method comprises passing the gas into a cavity in which is housed an electrical conductor supplied with direct current whereby an electrostatic field is generated between the electrical conductor and the walls of the cavity and whereby particles dispersed in the gas are deposited upon the walls of the cavity by the action of the electrostatic field; heating the walls of the cavity to vaporise the deposited particles; and determining the metal content of the vapour by an electrothermal atomic absorption method or by a spectrometric method.

2. A method according to claim 1, wherein the walls of the cavity are heated by the Joule effect.

3. A method according to claim 1 or 2, wherein the cavity is of cylindrical shape, and wherein the electrical conductor is an elongated electrical conductor disposed along the axis of the cylindrical cavity.

4. A method according to claim 3, wherein the ratio of the length to the diameter of the cylindrical cavity is from 5:1 to 50:1.

5. A method according to claim 4, wherein the ratio of the length to the diameter of the cylindrical cavity is from 8:1 to 20:1.

6. A method according to any of claims 1 to 5, wherein the metal content of the vapour is determined by disposing the cavity containing the vapour in an optical path between a cathode lamp and a photomultiplier monochromator.

7. A method according to any of claims 1 to 6, wherein the residence time of the gas in the cavity is from 0.02 to 2 seconds.

8. A method according to claim 7, wherein the residence time of the gas in the cavity is from 0.1 to 0.5 seconds.

9. A method according to any of claims 1 to 8, wherein the walls of the cavity are made of graphite.

10. A method according to any of claims 1 to 9, wherein the metal determined is lead, zinc or copper.

11. A method according to claim 1, substantially as hereinbefore described with reference to Figs. 1A and 1B of the accompanying drawing.

12. An apparatus for use in a method according to claim 1, comprising a cylindrical body defining a cylindrical cavity, and an elongated electrical conductor disposed along the axis of the cylindrical cavity.

13. An apparatus as claimed in claim 12, wherein the ratio of the length to the diameter of the cylindrical cavity is from 6:1 to 50:1.

14. An apparatus as claimed in claim 13, wherein the ratio of the length to the diameter of the cylindrical cavity is from 8:1 to 20:1.

15. An apparatus as claimed in any of claims 12 to 14, wherein the cylindrical body is made of graphite.

16. An apparatus for use in a method according to claim 1, substantially as hereinbefore described with reference to, and as shown in, Figs. 1A and 1B of the accompanying drawing.

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